

The Acceptor Properties of some Organophosphorus(v) Bromides

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The acceptor properties of the organophosphorus(v) bromides $\text{PBr}_3(\text{cat})$ (cat = benzene-1,2-diolate), $\text{PBr}(\text{cat})_2$, and PBr_4Ph , and of the PBr_3Ph^+ cation, towards Lewis bases such as halide ions and uni- or bi-dentate pyridines have been investigated, mainly by means of ^{31}P n.m.r. spectroscopy. Several new complexes have been isolated, and characterised by elemental analysis and (in some instances) n.m.r. or vibrational spectroscopy.

In recent years the acceptor properties of several chlorophosphorus(v) species, including PCl_5 ,¹ the PCl_4^+ ion,² PCl_4Ph ,³ $\text{PCl}_3(\text{cat})$ ⁴ (cat = benzene-1,2-diolate, $\text{C}_6\text{H}_4\text{O}_2$), $\text{PCl}(\text{cat})_2$,⁴ PCl_4Me ,⁵ PCl_4Et ,⁵ and derivatives thereof, towards the Lewis bases Cl^- and uni- or bi-dentate pyridines, have been described. The Lewis acid behaviour of phosphorus(v) bromide is not readily investigated, since it dissociates when dissolved in solvents of low polarity, equation (1), and is



stabilised (as the PBr_4^+ ion) only in polar, oxidising solvents such as liquid Br_2 or 25-oleum (containing 25% SO_3).⁶ The acceptor properties of the organophosphorus(v) bromides $\text{PBr}_3(\text{cat})$, $\text{PBr}(\text{cat})_2$, and PBr_4Ph , together with those of $[\text{PBr}_3\text{Ph}][\text{BBr}_4]$ towards halide ions and pyridine bases are now reported. There have been no previous studies in this area, although the formation of an adduct by $\text{PBr}(\text{cat})_2$ with a bidentate pyridine such as 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen) was expected to lead to the same cationic species $[\text{P}(\text{cat})_2\text{L}]^+$ (L = bipy or phen) as those formed by $\text{PCl}(\text{cat})_2$ under similar conditions.^{4,7} Several new compounds have been isolated and characterised by elemental analysis, ^{31}P n.m.r. spectroscopy (where possible), and in some cases vibrational spectroscopy.

Experimental

All manipulations, including n.m.r. sample preparation, were carried out either under an inert atmosphere of dry nitrogen or *in vacuo*. Chemicals of the best available commercial grade were used, in general without further purification except for tetra-alkylammonium chlorides which were dried as described previously.⁸ $\text{PBr}(\text{cat})$ was prepared by the method of Gross and Karsch,⁹ and $\text{PCl}(\text{cat})_2$ as described previously.^{4,10} The compound $\text{PBr}(\text{cat})_2$ was prepared by adding an excess of bromine to a solution of $\text{PCl}(\text{cat})_2$ in CH_2Cl_2 , giving rise to a very effervescent reaction. The solution was left to stir for a few minutes, and the solvent then removed *in vacuo* to give a white solid product (Found: C, 44.0; H, 2.5; Br, 24.5; P, 9.5. $\text{C}_{12}\text{H}_8\text{BrO}_4\text{P}$ requires C, 44.1; H, 2.5; Br, 24.4; P, 9.5%). Tetrabromo(phenyl)phosphorane, PBr_4Ph , was prepared by bromination of PBr_2Ph in an inert solvent (CH_2Cl_2), as described previously.⁶ The preparation of other new complexes is described below, and their elemental analyses are given in Table 1. Light petroleum used was that fraction boiling at 30–40 °C.

$[\text{PBr}_2(\text{cat})(\text{py})_2][\text{Br}_3]$ (py = pyridine).— $\text{PBr}(\text{cat})$ (0.76 g, 3.47 mmol) was dissolved in a small amount of CH_2Cl_2 , and bromine (0.2 cm³, 3.88 mmol) was added, with stirring, to produce a pale orange solution. Pyridine (0.56 cm³, 6.94 mmol) was added cautiously, and an orange precipitate was instantly

Table 1. Elemental analyses^a

Compound	Analysis (%)				
	C	H	N	P	Br
$[\text{PBr}_2(\text{cat})(\text{py})_2][\text{Br}_3]$	27.5 (27.6)	2.1 (2.0)	3.9 (4.0)	4.2 (4.4)	61.0 (57.3)
$[\text{PBr}_2(\text{cat})(\text{bipy})_2][\text{Br}_3]\text{Br}$	31.6 (31.3)	1.7 (2.0)	4.9 (4.6)	5.1 (5.0)	51.8 (52.0)
$[\text{PBr}_2(\text{cat})(\text{bipy})][\text{BBr}_4]$	24.1 (24.5)	1.6 (1.5)	3.5 (3.6)	3.9 (3.9)	59.6 (61.0)
$[\text{PBr}_2(\text{cat})(\text{phen})][\text{Br}_3]$	30.5 (30.1)	1.9 (1.7)	4.0 (3.9)	4.5 (4.3)	54.9 (55.6)
$[\text{N}(\text{n-C}_5\text{H}_{11})_4][\text{PBrCl}(\text{cat})_2]^b$	59.7 (58.1)	9.1 (7.9)	2.4 (2.1)	4.6 (4.7)	12.0 (12.1)
$\text{PBr}(\text{cat})_2\text{py}$	50.8 (50.3)	3.0 (3.2)	4.6 (3.4)	7.6 (7.6)	19.4 (19.7)
$[\text{P}(\text{cat})_2(\text{bipy})_2][\text{Br}_3]\text{Br}$	45.7 (46.9)	3.3 (2.9)	4.8 (5.0)	5.8 (5.5)	28.5 (28.4)
$[\text{P}(\text{cat})_2(\text{phen})_2][\text{Br}_3]\text{Br}$	48.2 (49.1)	3.1 (2.7)	4.4 (4.8)	5.3 (5.3)	26.0 (27.2)
$[\text{PBr}_3\text{Ph}(\text{bipy})][\text{BBr}_4]$	22.8 (23.0)	1.5 (1.6)	3.4 (3.4)	3.8 (3.7)	66.8 (67.0)
$[\text{PBr}_3\text{Ph}(\text{phen})][\text{BBr}_4]$	25.2 (25.2)	1.6 (1.5)	3.2 (3.3)	3.5 (3.6)	64.8 (65.2)

^a Calculated values are given in parentheses. ^b Cl, 5.3 (5.4%).

formed. The product was separated, washed with low-boiling light petroleum and dried *in vacuo* to give a fine orange powder.

$[\text{PBr}_2(\text{cat})(\text{bipy})_2][\text{Br}_3]\text{Br}$.—This salt was similarly prepared from $\text{PBr}(\text{cat})$ (1.298 g, 5.92 mmol), bromine (0.33 cm³, 6.40 mmol) and 2,2'-bipyridine (0.926 g, 5.93 mmol), the base being dissolved in the minimum quantity of CH_2Cl_2 before addition. The product was isolated as above as a bright orange solid.

$[\text{PBr}_2(\text{cat})(\text{bipy})][\text{BBr}_4]$.—A mixture of bromine and $\text{PBr}(\text{cat})$ in CH_2Cl_2 was prepared as above, and an equimolar quantity of BBr_3 was added to the solution, with stirring. A solution of 2,2'-bipyridine in CH_2Cl_2 was added, and the solution left to stir for 5 min. A yellow precipitate then formed, and was isolated in a similar manner to the above compounds.

$[\text{PBr}_2(\text{cat})(\text{phen})][\text{Br}_3]$.—Bromine (0.5 cm³, 9.70 mmol) was added, with stirring, to a solution of $\text{PBr}(\text{cat})$ (2.07 g, 9.45 mmol) in CH_2Cl_2 . A solution of 1,10-phenanthroline (1.708 g, 9.48 mmol) in the same solvent was then added slowly, with constant stirring. The yellow precipitate which immediately formed was isolated as above, washed with CH_2Cl_2 and low-boiling light petroleum and dried *in vacuo*.

$[\text{N}(\text{n-C}_5\text{H}_{11})_4][\text{PBrCl}(\text{cat})_2]$.— $\text{PBr}(\text{cat})_2$ (0.448 g, 1.37 mmol) was dissolved in a small amount of CH_2Cl_2 , and $\text{N}(\text{n-C}_5\text{H}_{11})_4\text{Cl}$

(0.463 g, 1.39 mmol) was added to the solution, with stirring. The solvent was removed *in vacuo* to yield a white solid.

PBr(cat)₂·py.—Pyridine was dripped into an equimolar quantity of PBr(cat)₂ dissolved in CH₂Cl₂, with stirring. The white precipitate which immediately formed was isolated as above and washed with low-boiling light petroleum.

[P(cat)₂(bipy)]₂[Br₃]Br.—PBr(cat)₂ was dissolved in CH₂Cl₂ and an equimolar quantity of 2,2'-bipyridine was added, with stirring. The yellow precipitate which immediately formed was isolated and washed as above. Analysis indicated the approximate composition [P(cat)₂(bipy)]₂⁺[Br₃]⁻Br⁻.

[P(cat)₂(phen)]₂[Br₃]Br.—This salt was prepared in a similar manner to the previous one, except that the 1,10-phenanthroline was dissolved in CH₂Cl₂ prior to addition. A yellow solution resulted, which when placed in a refrigerator overnight yielded a yellow precipitate. This was treated as above.

[PBr₃Ph][BBr₄].—An equimolar quantity of BBr₃ was added cautiously to a slurry of PBr₃Ph in CH₂Cl₂.⁶ The mixture was left to stir for 15 min, when a white precipitate was observed. The compound was isolated as above.

[PBr₃Ph(bipy)][BBr₄].—The salt [PBr₃Ph][BBr₄] was dissolved in CH₂Cl₂ and an equimolar quantity of 2,2'-bipyridine was added, with stirring. A yellow precipitate was observed. The solution was left to stir for 30 min, and the solid then isolated and washed in the usual manner.

[PBr₃Ph(phen)][BBr₄].—This salt was similarly prepared from [PBr₃Ph][BBr₄] and 1,10-phenanthroline. The yellow solid which separated immediately on mixing was isolated as above.

Phosphorus-31 n.m.r. spectra were recorded at 307.2 K on a Fourier-transform spectrometer, as described previously.⁸ Chemical shifts were measured relative to external H₃PO₄, with the downfield direction taken as positive. Boron-11 n.m.r. spectra were recorded at the same temperature on a multinuclear Fourier-transform spectrometer, which has been described before in relation to ¹¹⁹Sn n.m.r. spectra.¹¹ Chemical shifts are similarly expressed relative to external B(OMe)₃. Microanalyses (C, H, N, P, Cl, and Br) and i.r. spectra were obtained as described in earlier papers,^{6,8,12} while Raman spectra were recorded on a Cary 82 spectrometer by Mrs. J. Slegrova, using an argon laser.

Results and Discussion

(a) **PBr₃(cat).**—This compound was first prepared by Gross, Gloede and co-workers,^{13,14} and has been widely used in the preparation of acidic bromides.¹⁵ It was found to be soluble in most common organic solvents, and ³¹P chemical shifts of -188.6 p.p.m. in CS₂, -186.9 p.p.m. in CH₂Cl₂, -189.0 p.p.m. in CHCl₃, and -190.1 ± 1 p.p.m. in the solid state were measured, in excellent agreement with the previous solution value from CHCl₃.¹⁶ These shifts indicate that the compound has a five-co-ordinate molecular structure in both solid and solution.

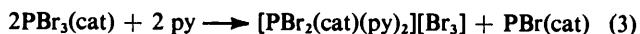
When a small amount of NBuⁿ₄Br was added to a solution of PBr₃(cat) in CH₂Cl₂, the ³¹P n.m.r. spectrum showed two peaks, at 197.6 and -195.1 p.p.m., the latter ascribed to starting material. Addition of more of the bromide resulted in the appearance of a single resonance at 196.7 p.p.m., which may be readily assigned to PBr(cat).¹⁶ These results suggest that PBr₃(cat) does not show acceptor properties towards the

bromide ion, unlike PCl₃(cat) which forms [PCl₄(cat)]⁻ with Cl⁻ ions,⁴ but decomposes to PBr(cat) with formation of the tribromide ion, equation (2). Analogous behaviour towards



Br⁻ ions is shown by both PBr₃¹⁷ and PBr₄Ph (see later).

Lewis acid characteristics were shown, however, towards pyridine bases. When a 1 : 1 : 2 mixture of PBr(cat), Br₂ [to form PBr₃(cat) *in situ*], and pyridine was prepared in CH₂Cl₂, an orange precipitate was immediately formed and no solution signals could be observed. The solid was isolated, and analysed as [PBr₂(cat)(py)₂][Br₃] (Experimental section). It did not give a solid-state spectrum, but in PhNO₂ showed a single sharp peak at -217.6 p.p.m. Although three geometrical isomers are possible for [PBr₂(cat)(py)₂]⁺, the observation of one resonance only suggests that either one isomer is formed preferentially, or else there is rapid exchange between the isomers. Similar behaviour has been observed for the [PCl₂(cat)(py)₂]⁺ cation, formed from [PCl₂(cat)][SbCl₆] and py.⁴ Confirmation of the presence of the Br₃⁻ ion was provided by the Raman spectrum, which showed a band at 168 cm⁻¹.¹⁸ Formation of Br₃⁻ implies some reduction of PBr₃(cat) to PBr(cat), equation (3). No signal was detected from the



phosphorus(III) species, possibly because the precipitate rapidly filled the coil region of the spectrometer probe. Since excess pyridine would also be present (because of the 1 : 1 : 2 molar ratio), an alternative possibility is weak complex formation between PBr(cat) and the base, giving rise to a broad exchange peak which may not have been detected. Similar behaviour, with formation of either mixed Br⁻ and Br₃⁻ counter ions, or Br₃⁻ alone as the counter ion, was found with bidentate pyridine bases, as indicated below.

A 1 : 1 : 1 mixture of PBr(cat), Br₂, and bipy in CH₂Cl₂ yielded an orange precipitate and a single ³¹P resonance at -198.2 p.p.m., assigned to the complex cation [PBr₂(cat)(bipy)]⁺. Again only one n.m.r. signal was seen, indicating the formation of one isomer only or rapid exchange between the two possible geometric isomers. The cation [PCl₂(cat)(bipy)]⁺ similarly gave a single peak only in CH₂Cl₂, although evidence for the existence of a second isomer was found from one experiment in PhNO₂ as solvent.⁴ When the same solution was monitored after 1 h, no signal could be detected. The solid product was isolated, and analysed as [PBr₂(cat)(bipy)]₂[Br₃]Br. The expected Raman band for the Br₃⁻ ion was observed at 173 cm⁻¹.¹⁸ The solid gave a broad ³¹P peak at -198 ± 3 p.p.m., in excellent agreement with the solution shift. The compound [PBr₂(cat)(bipy)][BBr₄] was also prepared; its solid-state ³¹P spectrum consisted of a broad peak at -193.5 ± 4 p.p.m., and in PhNO₂ it gave a single resonance at -195.1 p.p.m. Its i.r. spectrum between 650 and 250 cm⁻¹ (Nujol mull) was very similar to that of [PBr₂(cat)(bipy)]₂[Br₃]Br, except for an additional broad band at 590 cm⁻¹, readily assigned to the BBr₄⁻ ion.^{19,20} It gave a solid-state ¹¹B resonance at -53.5 p.p.m., in good agreement with the value of -52.5 p.p.m. reported for [NET₄][BBr₄],²¹ while the shift of -44.5 p.p.m. in PhNO₂ also agrees well with literature values²²⁻²⁴ for this ion in solution. A Raman frequency of 244 cm⁻¹ was ascribed to the BBr₄⁻ ion.²⁵

When an equimolar amount of 1,10-phenanthroline was added to a PBr(cat)-Br₂ mixture in CH₂Cl₂, a yellow precipitate was immediately formed and no ³¹P solution spectrum could be observed. The product was isolated, and analysed as [PBr₂(cat)(phen)][Br₃]. Unfortunately no solid-state n.m.r. signals could be detected from this salt. A Raman band at

Table 2. I.r. frequencies (650–400 cm^{-1}) for $\text{PBr}(\text{cat})_2$ and related species

Compound	ν/cm^{-1}
$\text{PBr}(\text{cat})_2$	636s, 590w, 578s, 552br, 538w, 504br, 470w, 420s, 400w
$[\text{PBrCl}(\text{cat})_2]^-$	624s, 584m, 572s, 560w, 530s, 500s, 470br, 430m, 420w
$[\text{PCl}_2(\text{cat})_2]^-$ *	640s, 628w, 590m, 578m, 562w, 550w, 540m, 530w, 500s, 470w, 460s, 430s

* Ref. 4.

168 cm^{-1} was ascribed to a vibration of a symmetrical tri-bromide ion,¹⁸ although different frequencies have been reported for unsymmetrical Br_3^- ions.²⁶

The results thus show that $\text{PBr}_3(\text{cat})$ possesses Lewis acid properties towards pyridine bases, resulting in the formation of six-co-ordinate cations. Similar compounds were formed by bipy and phen with $\text{PCl}_3(\text{cat})$, but the molecular species $\text{PCl}_3(\text{cat})\cdot\text{py}$ (both isomers) was formed preferentially by py, even though $[\text{PCl}_2(\text{cat})(\text{py})_2]^+$ was also present.⁴ With $\text{PBr}_3(\text{cat})$ the ionic form $[\text{PBr}_2(\text{cat})(\text{py})_2]^+$ is clearly favoured by rapid precipitation of the complex from CH_2Cl_2 .

(b) $\text{PBr}(\text{cat})_2$.—This compound had not been reported previously in the literature, but was prepared as described in the Experimental section. It was readily soluble in organic solvents, and ^{31}P chemical shifts of -27.5 p.p.m. in CH_2Cl_2 and -29.1 p.p.m. in PhNO_2 were recorded, as well as a broad solid-state resonance at -29.1 p.p.m. These results suggest a five-co-ordinate molecular structure for the compound, possibly similar to that of $\text{PCl}(\text{cat})_2$.²⁷

When NBu^n_4Br was added to a solution of $\text{PBr}(\text{cat})_2$ in CH_2Cl_2 , a slight upfield movement of the single resonance to -29.1 p.p.m. was observed. This was not considered significant, and no further upfield shift took place on addition of excess Br^- ions, indicating that $[\text{PBr}_2(\text{cat})_2]^-$ is not formed under the experimental conditions. The route of decomposition to a phosphorus(III) compound, with formation of Br_3^- ions, is not open to $\text{PBr}(\text{cat})_2$. Rather surprisingly, however, $\text{PBr}(\text{cat})_2$ showed acceptor properties towards chloride ions. Addition of $\text{N}(\text{n-C}_5\text{H}_{11})_4\text{Cl}$ to a solution of $\text{PBr}(\text{cat})_2$ in PhNO_2 caused the single ^{31}P peak to move upfield, and a limiting shift of -69.5 p.p.m. was established, ascribed to the $[\text{PBrCl}(\text{cat})_2]^-$ ion. A white solid isolated from equimolar amounts of $\text{N}(\text{n-C}_5\text{H}_{11})_4\text{Cl}$ and $\text{PBr}(\text{cat})_2$ analysed as $[\text{N}(\text{n-C}_5\text{H}_{11})_4][\text{PBrCl}(\text{cat})_2]$. No solid-state n.m.r. signal could be obtained, but its i.r. spectrum between 650 and 400 cm^{-1} showed marked differences from that of $\text{PBr}(\text{cat})_2$, and also differed from that⁴ of $[\text{PCl}_2(\text{cat})_2]^-$ (Table 2). $\text{PCl}(\text{cat})_2$ similarly showed acceptor properties towards chloride ions, and salts containing the $[\text{PCl}_2(\text{cat})_2]^-$ ion have been isolated,⁴ but its reaction with bromide ions was not investigated.

When pyridine was added to a dilute solution of $\text{PBr}(\text{cat})_2$ in CH_2Cl_2 , a single ^{31}P resonance was found at -85.5 p.p.m., attributed to the molecular species $\text{PBr}(\text{cat})_2\cdot\text{py}$, or an equilibrium peak between $\text{PBr}(\text{cat})_2$ and $\text{PBr}(\text{cat})_2\cdot\text{py}$.^{4,7} Although two isomers are possible for $\text{PBr}(\text{cat})_2\cdot\text{py}$, the observation of a single peak suggests either preferential formation of one isomer or a rapid equilibrium between them. Similar behaviour has been observed in the $\text{PCl}(\text{cat})_2\text{-py}$ system, although in this case the ionic species $[\text{P}(\text{cat})_2(\text{py})_2]^+$ was also detected.^{4,7} The solution deposited a white solid after some time, and the solution signal disappeared, showing that complete reaction had occurred. When the experiment was repeated on a preparative scale using more concentrated

Table 3. I.r. frequencies (650–250 cm^{-1}) of some Lewis base derivatives of $\text{PBr}(\text{cat})_2$

Compound	ν/cm^{-1}
$\text{PBr}(\text{cat})_2\cdot\text{py}$	650s, 620w, 610w, 586w, 572m, 546s, 510w, 504m, 460m, 426s, 366br, 320m, 306w
$[\text{P}(\text{cat})_2(\text{bipy})]_2[\text{Br}_3]\text{Br}$	640s, 616s, 564s, 542s, 526m, 480s, 460w, 440m, 432s, 416w, 400m, 350m, 320w, 300w, 290w, 284w
$[\text{P}(\text{cat})_2(\text{phen})]_2[\text{Br}_3]\text{Br}$	646s, 626s, 600s, 572m, 564m, 510s, 500s, 472s, 450s, 438s, 400w, 390w, 350m, 330w, 300w, 280w

solutions, the precipitate formed immediately. It analysed as the 1:1 molecular adduct $\text{PBr}(\text{cat})_2\cdot\text{py}$, but failed to give a solid-state ^{31}P n.m.r. spectrum.

Addition of either bipy or phen to a solution of $\text{PBr}(\text{cat})_2$ in CH_2Cl_2 resulted in a yellow precipitate, instantly in the case of bipy where no solution peak was apparent. Two resonances were found for the phen solution, however, at -29.1 [$\text{PBr}(\text{cat})_2$] and -90.4 p.p.m. The higher field resonance was assigned to the $[\text{P}(\text{cat})_2(\text{phen})]^+$ cation, and is in good agreement with the reported value of -89.9 p.p.m. for $[\text{P}(\text{cat})_2(\text{phen})][\text{SbCl}_6]$ in PhNO_2 .⁴ When more phen was added, the peak from the starting material disappeared, showing that reaction was complete. Only the bipy adduct gave a solid-state signal, at -85.5 ± 2 p.p.m. This compares with a solution shift of -93.4 p.p.m. for $[\text{P}(\text{cat})_2(\text{bipy})][\text{SbCl}_6]$ in PhNO_2 .⁴ {A larger difference between solid-state and solution shifts has been observed previously⁴ for $[\text{P}(\text{cat})_2(\text{phen})]^+$.} Both solid complexes analysed approximately as $[\text{P}(\text{cat})_2\text{L}]_2[\text{Br}_3]\text{Br}$ (L = bipy or phen). The formation of the Br_3^- ion in these reactions is rather puzzling, since the only source of bromine was $\text{PBr}(\text{cat})_2$, and there is no ready route for its decomposition to a phosphorus(III) species, unlike $\text{PBr}_3(\text{cat})$, PBr_4Ph , or PBr_5 . The Raman spectrum of the phen complex showed the expected band for Br_3^- at 167 cm^{-1} .¹⁸ The i.r. spectra of the adducts with pyridine bases differed appreciably from that of $\text{PBr}(\text{cat})_2$ below 650 cm^{-1} , and the frequencies are listed in Table 3.

Hence $\text{PBr}(\text{cat})_2$ shows acceptor properties towards Cl^- ions, py, bipy, and phen, but not towards Br^- ions under the experimental conditions. Its reactions with pyridine bases appear to be simpler than those of $\text{PCl}(\text{cat})_2$, with only a single phosphorus-containing species being formed in each instance, possibly stabilised by rapid precipitation in the case of py. The bidentate ligands seem to displace Br^- readily, unlike $\text{PCl}(\text{cat})_2$ where phen in particular reacted very slowly,⁴ although it was noticeable here that precipitation of the complex was much faster with bipy than with phen. The apparent instability of $[\text{PBr}_2(\text{cat})_2]^-$ explains the non-observation of a second exchanging peak, as was found in the $\text{PCl}(\text{cat})_2\text{-bipy}$ reaction.⁴

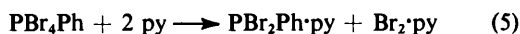
(c) PBr_4Ph and $[\text{PBr}_3\text{Ph}][\text{BBr}_4]$.—Tetrabromo(phenyl)-phosphorane was first prepared by Michaelis and Köhler,²⁸ and may be readily obtained by bromination of PBr_2Ph in an inert solvent.⁶ A chemical shift of 23.0 p.p.m. in 25-oleum has been ascribed to the PBr_3Ph^+ cation, which is also known in salts such as $[\text{PBr}_3\text{Ph}][\text{BBr}_4]$, and in admixture with the other cations in the series $[\text{PCl}_n\text{Br}_{3-n}\text{Ph}]^+$.⁶ The solid-state spectrum of the compound consisted of a broad resonance at 14.6 p.p.m., with apparent shoulders at 22.7 and 1.6 p.p.m., suggesting an ionic structure $[\text{PBr}_3\text{Ph}]^+\text{Br}^-$, similar to that of PBr_5 . The compound was found to be insoluble in common organic

solvents, and no solution data could be obtained, providing further support for an ionic rather than a covalent formulation.

When bromide ions (in the form NR_4Br) were added to a slurry of PBr_4Ph in CH_2Cl_2 or PhNO_2 , the only ^{31}P signal observed was at 153.1 p.p.m., readily assigned to PBr_2Ph .²⁹ The solutions were red, suggesting that reaction (4) occurs



readily. This parallels the reactions of PBr_3 and $\text{PBr}_3(\text{cat})$ with bromide ions. A solution of PBr_4Ph in neat pyridine gave a single resonance at 146.0 p.p.m., slightly to high field of the literature value for PBr_2Ph .²⁹ Similarly the addition of excess pyridine to a slurry of PBr_4Ph in CH_2Cl_2 led to a signal at 148.4 p.p.m. This upfield movement relative to PBr_2Ph could be due to weak complex formation between PBr_2Ph and py, equation (5), similar to that found for PCl_3 and py where a



single exchanging peak was detected.¹ No bromine colour was observed, possibly because of formation of the pyridine-bromine adduct, as shown in equation (5). When either bipy or phen was added to a slurry of PBr_4Ph in CH_2Cl_2 or PhNO_2 , no solution signals were detected, but a yellow precipitate separated. The product was prepared and isolated from CH_2Cl_2 in both instances, but analysed as PBr_4Ph , as well as giving an identical i.r. spectrum to the starting material. The results indicate that under the experimental conditions PBr_4Ph has no acceptor properties towards pyridine bases, unlike PCl_4Ph which forms stable six-co-ordinate compounds.³

The salt $[\text{PBr}_3\text{Ph}][\text{BBr}_4]$ was isolated as a white solid from stoichiometric amounts of PBr_4Ph and BBr_3 . It gave a ^{31}P shift of 24.2 p.p.m. in PhNO_2 , and a broad resonance at 21.1 p.p.m. in the solid state. Its ^{11}B solution spectrum in PhNO_2 consisted of a single peak at -38.9 p.p.m., close to literature values for the BBr_4^- ion,²²⁻²⁴ and the solid gave a broad signal, also at -38.9 p.p.m. Its i.r. spectrum was similar to that of PBr_4Ph , except for an additional broad band at 584 cm^{-1} , ascribed to the BBr_4^- ion.^{19,20} Addition of stoichiometric quantities of either bipy or phen to a solution of $[\text{PBr}_3\text{Ph}][\text{BBr}_4]$ in PhNO_2 caused the appearance of a yellow precipitate, and no solution signals could be detected. The bipy complex was obtained on a preparative scale from CH_2Cl_2 solution as a yellow solid, which analysed as a 1 : 1 adduct and is formulated as $[\text{PBr}_3\text{Ph}(\text{bipy})][\text{BBr}_4]$. No solid-state ^{11}B spectrum could be obtained for the complex, and the only signal in the corresponding ^{31}P spectrum was a sharp peak at -1.6 p.p.m., ascribed to an impurity since a resonance at much higher field is expected for the cation. It gave a single ^{11}B resonance in PhNO_2 solution at -42.3 p.p.m., assigned to the BBr_4^- ion.²²⁻²⁴ The phen complex was similarly isolated, and analysed as $[\text{PBr}_3\text{Ph}(\text{phen})][\text{BBr}_4]$. No solid-state ^{31}P signal was found, but a broad ^{11}B resonance at -37.7 p.p.m. was detected, similar to values for other tetrabromoborates, although some variation with the cation has been observed.²¹ The compound was insoluble in all common solvents attempted, and no solution data could be obtained. Despite these limitations, there is clear evidence for the formation of (presumably six-co-ordinate) compounds in these systems, showing that the $[\text{PBr}_3\text{Ph}]^+$ cation does possess some acceptor properties. The complexes were probably stabilised in this instance by rapid precipitation. It is plain, nevertheless, that the Lewis acid properties of PBr_4Ph and its derivatives are markedly inferior to those of their chloro-analogues,³ as reflected in the different structures of the phosphoranes themselves, where PCl_4Ph is molecular in the solid³⁰ and PBr_4Ph has a phosphonium salt structure.

The results overall show that several six-co-ordinate phosphorus(v) compounds with bromide ligands present may be prepared, but their stability is generally lower than that of analogous chloro-compounds unless rapid precipitation occurs. Anionic complexes in particular are noticeably reluctant to form, partly because of competing reactions between some bromophosphoranes [PBr_3 , $\text{PBr}_3(\text{cat})$, PBr_4Ph] and bromide ions. $[\text{PBr}_2(\text{cat})_2]^-$ ions were not encountered under the experimental conditions, but $\text{PBr}(\text{cat})_2$ did show acceptor properties towards chloride ions.

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